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# Variational calculation of highly excited rovibrational energy levels of $\text{H}_2\text{O}_2$

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## Abstract

Results are presented for highly accurate *ab initio* variational calculation of the rotation - vibration energy levels of  $\text{H}_2\text{O}_2$  in its electronic ground state. These results use a recently computed potential energy surface and the variational nuclear-motion programmes WARV4, which uses an exact kinetic energy (EKE) operator, and TROVE, which uses a numerical expansion for the kinetic energy. The TROVE calculations are performed for levels with high values of rotational excitation,  $J$  up to 35. The purely *ab initio* calculations of the rovibrational energy levels reproduce the observed levels with a standard deviation of about  $1\text{ cm}^{-1}$ , similar to that of the  $J = 0$  calculation as the discrepancy between theory and experiment for rotational energies within a given vibrational state is substantially determined by the error in the vibrational band origin. Minor adjustments are made to the *ab initio* equilibrium geometry and to the height of the torsional barrier. Using these and correcting the band origins using the error in  $J = 0$  states lowers the standard deviation of the observed – calculated energies to only  $0.002\text{ cm}^{-1}$  for levels up to  $J = 10$  and  $0.02\text{ cm}^{-1}$  for all experimentally known energy levels, which extend up to  $J = 35$ .

## 1 Introduction

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is a well-studied system because of its unusual properties, particularly the almost freely rotating OH moieties. The role of  $\text{H}_2\text{O}_2$  in the chemistry of the Earth's atmosphere<sup>1–3</sup> as well as of the Martian atmosphere<sup>4,5</sup> has been widely acknowledged. It has also recently been detected in the interstellar medium.<sup>6</sup> The vibration-rotation spectra of hydrogen peroxide has attracted

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significant attention, both experimental and theoretical. For example it has been used as a benchmark system with large amplitude motion for testing different variational nuclear motion codes.<sup>7–15</sup>

Very recently Malyszczek and Koput<sup>16</sup> presented a highly accurate *ab initio* potential energy surface (PES) of HOOH which was shown to reproduce the known vibrational band origins with the average accuracy of 1 cm<sup>-1</sup>. Other *ab initio* PESs of HOOH were reported by Harding,<sup>17</sup> Kuhn *et al.*,<sup>18</sup> Senent *et al.*,<sup>19</sup> and Koput *et al.*<sup>20</sup>

Hydrogen peroxide has three important properties from the viewpoint of variational calculations. Firstly, the large amplitude motion of the OH internal rotors that has already been mentioned. Secondly, its relatively low dissociation energy of about 17,000 cm<sup>-1</sup> has made H<sub>2</sub>O<sub>2</sub> a benchmark tetratomic molecule for experimental study of the dissociation process.<sup>21</sup> Thirdly, H<sub>2</sub>O<sub>2</sub> is a tetratomic system where variational calculations can really aid the analysis of spectra.

For triatomic molecules, accurate calculation of the rotation-vibration levels to high accuracy using variational nuclear motion methods has become routine.<sup>22–24</sup> For tetratomic molecules this process is just beginning; it is natural for initial high accuracy studies to focus on molecules with large amplitude motion such as ammonia<sup>25,26</sup> and hydrogen peroxide.

The advantages of using variational calculations to assign vibration-rotation spectra of triatomic molecules has been demonstrated for several molecules. Initial studies focused on H<sub>3</sub><sup>+</sup><sup>27–29</sup> and water,<sup>30,31</sup> systems for which the use of variational calculations to analyse spectra is now the accepted procedure. In particular, spectra involving hot molecules, and hence high rotational states, and large amplitude motion, such as H<sub>3</sub><sup>+</sup> on Jupiter<sup>27</sup> and water on the Sun,<sup>30</sup> assignments using the traditional, effective Hamiltonian approach are almost impossible.

A significant advantage of variational calculations over effective Hamiltonian techniques is the automatic allowance for accidental resonances between vibrations. Whereas for most triatomic molecules such resonances become significant at fairly high vibrational energies, for tetratomic molecules accidental resonances can even make the analysis of low-lying vibrational states intractable using effective Hamiltonians. H<sub>2</sub>O<sub>2</sub> is a good example of this situation. Although H<sub>2</sub>O<sub>2</sub> spectral lines are strong and were first observed more than seventy years ago with spectrometers much less sophisticated than those available nowadays,<sup>32,33</sup> the analysis of experimental spectra involving high *J* transitions for H<sub>2</sub>O<sub>2</sub> is only complete up to 2000 cm<sup>-1</sup>,<sup>34–36</sup> significantly lower in frequency than transitions to the OH stretching fundamentals. One reason for this is the complication of the analysis by accidental resonances. Accurate variational calculations on H<sub>2</sub>O<sub>2</sub> offer a way out of this impasse.

Recent advances in variational calculations suggest that they can be used for systems larger than triatomic. High accuracy variational calculations of the spectra and line lists for tetratomic molecules such as ammonia<sup>26,37,38</sup> have been performed. These NH<sub>3</sub> line lists have been used both for the

assignment of transitions involving higher vibrational states,<sup>39</sup> hot rovibrational spectra involving high  $J$  levels<sup>40</sup> as well as for correcting and improving the analysis of more standard transitions.<sup>26,41</sup> Numerical calculations of wavefunctions for high  $J$  states of tetratomic molecules are possible not only because modern computers have the ability to diagonalise larger matrices but also because, as illustrated below, the accuracy of calculations employing approximate kinetic energy operators<sup>42,43</sup> becomes comparable with those using an exact kinetic energy approach.<sup>44</sup> While high  $J$  calculations within the exact kinetic energy approach are still computationally challenging for tetratomic molecules, calculations with  $J \sim 50$  are feasible with approaches such as TROVE.<sup>43</sup> Furthermore, the possibility of calculating *ab initio* dipole moment surfaces of extremely high accuracy<sup>45</sup> enhances the value of using variational calculations since they can also be used to create line lists. These factors raise the possibility of creating accurate line lists for H<sub>2</sub>O<sub>2</sub>. However, the presence of the large amplitude, torsional motion of the two OH fragments in H<sub>2</sub>O<sub>2</sub> complicates the problem. This requires an appropriate nuclear motion programme for calculation of the rovibrational energy levels by solving the corresponding Schrödinger equation; this programme should be able to compute high  $J$  levels within the limitations of the modern computers.

In this paper we compute high accuracy rovibrational energy levels going to high  $J$  for H<sub>2</sub>O<sub>2</sub> using the *ab initio* PES due to Małyszczek and Koput.<sup>16</sup> To do this we test two nuclear motion programmes: the exact kinetic energy (EKE) programme WAVR4<sup>46</sup> and approximate kinetic energy programme TROVE.<sup>43</sup> It is shown that use of TROVE allows us to calculate very high  $J$  energy levels which are in excellent agreement with observation. The paper is organised as follows. Section 2 describes the modifications of the TROVE programme necessary to make it suitable for the calculation of spectra of such a nonrigid molecule. Section 3 describes the details of computations performed. Section 4 presents our results which is followed by the concluding section which discusses prospects for further work on this system.

## 2 Methods of calculation

The accuracy of a calculation of rovibrational energy levels depends first of all on the accuracy of the potential energy surface (PES) used as input to the nuclear motion Schrödinger equation. Until recently the most accurate PES for H<sub>2</sub>O<sub>2</sub> was the one due to Koput *et al.*<sup>20</sup> which gave a typical discrepancy between theory and experiment for vibrational band origins of about 10 cm<sup>-1</sup>.<sup>47</sup> However, two of us<sup>16</sup> recently determined a very accurate PES computed using the explicitly correlated coupled-cluster method [CCSD(T)-F12] method,<sup>48,49</sup> in the F12b form<sup>50</sup> as implemented in the MOLPRO package.<sup>51</sup> Various correlation-consistent basis sets were used for various parts of the PES, the largest being aug-cc-pV7Z. The CCSD(T)-F12 results were augmented with the Born-Oppenheimer diagonal,

higher-order valence-electron correlation, relativistic, and core-electron correlation corrections. The 1762 *ab initio* points obtained were fitted to the functional form

$$V(q_1, q_2, q_3, q_4, q_5, q_6) = \sum_{ijklmn} c_{ijklmn} q_1^i q_2^j q_3^k q_4^l q_5^m \cos nq_6 \quad (1)$$

where  $q_i$  ( $i = 1, 2, 3$ ) are the Simons-Parr-Finlan stretching OO and OH coordinates<sup>52</sup>  $q_1 = (R - R_e)/R$  and  $q_i = (r_i - r_e)/r$  ( $i = 1, 2$ ),  $q_4 = \theta_1 - \theta_e$  and  $q_5 = \theta_2 - \theta_e$  are the two OOH bending coordinates,  $q_6 = \tau$  is the torsional angle  $\angle\text{HOOH}$  (see Fig. 1), and  $R_e$ ,  $r_e$ , and  $\theta_e$  are the corresponding equilibrium values. The expansion coefficients  $c_{ijklmn}$  used in this work are given in the supplementary material<sup>53</sup> to this article (see also Ref. 16).

Recent calculations<sup>16</sup> using this PES gave, for the 30 observed vibrational band origins of  $\text{H}_2\text{O}_2$ , a standard deviation for the observed minus calculated (obs – calc) wavenumbers of about  $1 \text{ cm}^{-1}$ , an order of magnitude improvement over the previous results.<sup>47</sup> An *ab initio* line list with this accuracy could be useful for a number of applications. However, for most applications it is also necessary to accurately compute highly excited rotational levels. This is done in this work. Before looking at high  $J$  rotational levels, we reconsidered the  $J = 0$  results of Małyszczek and Koput<sup>16</sup> using both EKE programme WAVR4<sup>46</sup> and approximate kinetic energy programme TROVE.<sup>43</sup>

Diatom-diatom HO–OH coordinates were employed in the programme WAVR4; these coordinates were one of those used to consider acetylene – vinylidene isomerisation.<sup>54</sup> The calculations used a discrete variable representations (DVR) based on a grid of 10 radial functions for each OH coordinate and 18 radial functions for the OO coordinate. The parameters used for OH stretch Morse-oscillator like functions were  $r_e = 0.91 \text{ \AA}$ ,  $\omega_e = 2500 \text{ cm}^{-1}$  and  $D_e = 35000 \text{ cm}^{-1}$ , and  $r_e = 1.53 \text{ \AA}$ ,  $\omega_e = 1500 \text{ cm}^{-1}$  and  $D_e = 45000 \text{ cm}^{-1}$  for the OO stretch. The bending basis set consists of coupled angular functions<sup>46</sup> defined by  $j^{\text{max}} = l^{\text{max}} = 22$  and  $k^{\text{max}} = 12$ . The resulting energy levels with  $J = 0$  were within  $0.1 \text{ cm}^{-1}$  of the previous calculations,<sup>16</sup> see Table 2. However for WAVR4 calculations of the same accuracy for levels with  $J = 1$  require about 10 times more computer time. This is a consequence of the  $J - K$  coupling used in the EKE procedure. This coupling is essential for the linear HCCH system<sup>54</sup> and very floppy molecules,<sup>44</sup> but not for  $\text{H}_2\text{O}_2$ . The use of WAVR4 to calculate energies of high  $J$  levels is computationally unrealistic at present and we note that indeed corresponding studies on acetylene have thus far been confined to low  $J$  values.<sup>55</sup>

TROVE is a computer suite for rovibrational calculations of energies and intensities for molecules of (at least in principle) arbitrary structures. TROVE uses a multilevel contraction scheme for constructing the rovibrational basis set. The primitive basis functions are given by products of six 1-dimensional (1D) functions  $\phi_i(\xi_i)$ , where  $\xi_i$  represents one of the six internal coordinates. For HOOH we choose  $\xi_1$ ,  $\xi_2$ , and  $\xi_3$  to be the linearized versions of the three stretching internal displacements  $R - R_e$ ,  $r_1 - r_e$ ,

and  $r_2 - r_e$ , respectively,  $\xi_4$  and  $\xi_5$  are the linearized versions of the two bending displacements  $\theta_1 - \theta_e$  and  $\theta_2 - \theta_e$ ;  $\xi_6$  is the torsional coordinate  $\tau$ , see Fig. 1.

The kinetic energy operator in TROVE is given by an expansion in terms of the five coordinates  $\xi_i$ , representing the rigid modes  $i = 1 \dots 5$ . The potential energy function is also expanded but using three Morse-type expansion variables  $1 - \exp(-a_i \xi_i)$  ( $i = 1, 2, 3$ ) and two bending coordinates  $\xi_4$  and  $\xi_5$ . Here  $a_1 = 2.2 \text{ \AA}^{-1}$ ,  $a_2 = a_3 = 2.3 \text{ \AA}^{-1}$  were selected to match closely the shape of the *ab initio* PES along the stretching modes. In the present work we employ 6th and 8th order expansions to represent, respectively, the kinetic energy operator and potential energy function.

The rovibrational motion of the non-rigid molecule HOOH is best represented by the extended  $C_{2h}^+(M)$  molecular symmetry group,<sup>56</sup> which is isomorphic to  $D_{2h}(M)$  as well as to the extended group  $G(4)(EM)$ .<sup>57</sup> As explained in detail by Bunker and Jensen,<sup>57</sup> the extended group is needed to describe the torsional splitting due both the *cis*- and *trans*-tunnelings. In the present work we use the  $D_{2h}(M)$  group to classify the symmetry of the HOOH states. This group is given by the eight irreducible representations  $A_g, A_u, B_{1g}, B_{1u}, B_{2g}, B_{2u}, B_{3g}, B_{3u}$ . In order to account for the extended symmetry properties of the floppy HOOH molecules an extended range for torsion motion, from  $0^\circ$  to  $720^\circ$  was introduced into TROVE. In this representation  $\tau = 0$  and  $720^\circ$  correspond to the *cis* barrier, while at  $\tau = 360^\circ$  the molecule has the *trans* configuration.

TROVE's primitive basis functions,  $\phi_{v_i}^{(i)}$  ( $i = 1 \dots 6$ ), are generated numerically by solving six 1D vibrational Schrödinger equations for each vibrational mode  $i$  employing the Numerov-Cooley method.<sup>58,59</sup> The corresponding reduced 1D Hamiltonian operators  $H_i^{1D}$  ( $i = 1 \dots 6$ ) are obtained by freezing the five remaining modes at the corresponding equilibriums. The integration ranges are selected to be large enough to accommodate all basis functions required (see below for the discussion of the basis set sizes). The torsional functions are obtained initially on the range  $\tau = 0 \dots 360^\circ$  and transform according with the  $C_{2h}(M)$  group. A very fine grid of 30,000 points and the quadruple numerical precision [real(16)] was used for generating the eigenfunctions of the corresponding Schrödinger equation in order to resolve the *trans* splittings up to  $v_6 = 42$ . The wavefunctions are then extended to  $\tau = 360 \dots 720^\circ$  through the  $+/-$  reflection of the  $C_{2h}(M)$  values and classified according to  $D_{2h}(M)$ . The extended primitive torsion functions are able to account for the torsional splitting due to both the *cis* and *trans* tunneling.

The 6D primitive basis functions are then formed from different products of the 1D functions  $\phi_{v_i}^{(i)}$ . The size of the basis set is controlled in TROVE by the so-called polyad number  $P$ , which in the present case is given by

$$P = 4v_1 + 8(v_2 + v_3) + 8(v_4 + v_5) + v_6 \leq P_{\max}, \quad (2)$$

where  $v_i$ ,  $i = 1 \dots 6$  are the local mode quantum numbers corresponding to the primitive functions

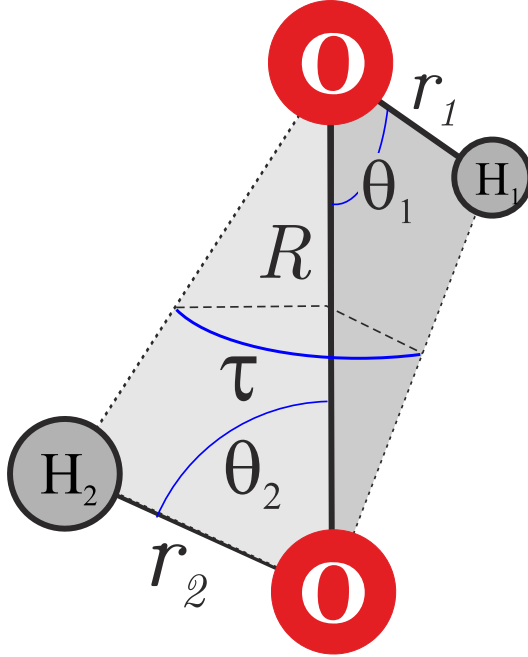


Figure 1: The internal coordinates for the HOOH molecule.

$\phi_{v_i}^{(i)}(\xi_i)$ . The primitive basis set is then processed through a number of contractions, as described in detail previously,<sup>37</sup> to give a final basis set in the  $J = 0$  representation.

Calculations using programme TROVE started with a search for a basis set and operator expansions which would give results close to the EKE ones. The final values of the basis set parameters were chosen to try to meet two conflicting requirements: the best possible convergence and a compact enough calculation to allow high  $J$  energy levels to be computed. The final basis set parameters were the following: the maximum polyad number  $P_{\max} = 42$ , which also corresponds to the highest excitation of the torsional mode  $v_6$ . For O-O stretch the maximal number was 8, for OH stretches - 8 and for the bending modes - 10. These parameters control the size of the basis set used in the TROVE calculations according with Eq. (2). For the  $J = 0$  levels they give good agreement with the previous studies, see Table 1.

### 3 Results

The updated version of TROVE was used to calculate excited rotational levels for  $J$  up to 35, the highest assigned thus far experimentally. Initial calculations were performed with the equilibrium distances and angles obtained *ab initio* in Ref. 16. In this case the discrepancies between theory

and experiment increased quadratically with increasing  $J$ : the  $J = 1$  levels were calculated with an accuracy around  $0.001 \text{ cm}^{-1}$ , but those for  $J = 35$  differ from experiment by about  $1 \text{ cm}^{-1}$ .

We therefore chose to adjust the equilibrium parameters  $R_e$  and  $r_e$  to better reproduce the experimental values. Only very small changes were needed to make the  $J = 35$  levels accurate to about  $0.03 \text{ cm}^{-1}$  for the ground vibrational state. In particular, the original value of  $R_e$  of  $1.45539378 \text{ \AA}$  was shifted to  $1.45577728 \text{ \AA}$  and  $r_e = 0.96252476 \text{ \AA}$  moved to  $0.96253006 \text{ \AA}$ . The rotational structure within the excited vibrational states is of similar accuracy, meaning that these levels are essentially shifted just by the discrepancy in the vibrational band origin. In practice this geometry shift not only meant that low  $J$  energy levels were reproduced with an accuracy of  $1 \text{ cm}^{-1}$ , reproducing the accuracy of the vibrational band origin, but also resulted in pseudo-resonance artifacts. To illustrate this consider the interaction between the ground vibrational state and the low-lying  $v_4 = 1$  torsional vibrational state, which lies about  $2 \text{ cm}^{-1}$  too low in the calculations. This results in an artificial closeness, and interaction, between levels with the same  $J$  and  $K_a = 8$  for  $v = 0$  and  $K_a = 6$  for  $v_4 = 1$ . The resulting shift in the energy levels is significant; it grows with  $J$  and reaches about  $1 \text{ cm}^{-1}$  at  $J = 30$ . We call this a pseudo-resonance artifact since no such interaction is seen in the experimentally-determined energy levels.

There are several ways to avoid this artificial pseudo-resonances. One would be to fit the PES to experimental data, which would remove this artificial near-degeneracy. This is likely to be a topic of future work. An alternative possibility, which is already available within TROVE,<sup>37</sup> is to simply adjust the calculated values of the vibrational band origins given by the  $J = 0$  calculation to the observed ones prior to their use in calculations of the  $J > 0$  levels. This option, which is not available in EKE codes which couple the bending basis with the rotational functions,<sup>60</sup> not only shifts the energies, it also rearranges the matrix elements so that the artificial resonances disappear. With this adjusted calculation the energy levels vary smoothly with the increasing  $J$  and  $K_a$  quantum numbers, see Tables 2, 6 and 8, as one would expect<sup>61</sup> from purely *ab initio* levels.

One other problem remained when comparing our rotationally excited energy levels with the observed ones. This concerned rotational levels with the quantum number  $K_a = 1$  which did not behave as levels associated with other values of  $K_a$ . The error for the two levels with  $K_a = 1$  increases disproportionately to that of other levels as  $J$  increases. This error was about  $0.1 \text{ cm}^{-1}$  for  $J = 30$ . A series of test calculations revealed the reason for such discrepant behaviour of the levels with  $K_a = 1$ . It transpires that a small change in the height of the torsional barrier, which is strongly influenced by the linear expansion coefficient  $c_{000001}$ , does not affect other  $K_a$  levels, but significantly influences only those with  $K_a = 1$ . Varying this expansion coefficient can both increase and decrease the splitting of the  $K_a = 1$  doublet. As this splitting is overestimated in calculations using the *ab initio* value of



$c_{000001}$ , its reduction by about 1 % from the *ab initio* value of 0.00487 to 0.00483  $E_h$  results in roughly a fourfold improvement of the obs – calc value for the  $K_a = 1$  levels. This change affects the value of the ground-state torsional splitting of 11  $\text{cm}^{-1}$  and also the values of the other torsional energy levels, all of which move significantly closer to the observed values, than the purely *ab initio* levels given in the Table 1. In particular, this small adjustment improves the calculated ground-state splitting to 11.4  $\text{cm}^{-1}$  and the first torsional level to 255.2  $\text{cm}^{-1}$ . Thus adjusting  $c_{000001}$  not only improves significantly the values of levels with  $K_a = 1$  levels, it improves the overall agreement with experiment for the band origins. The underlying reason for this is that the expansion coefficient  $c_{000001}$  controls the height of the torsional barrier.

These minor adjustments result in very accurate values for rotational energy levels a sample of which are presented in Tables 2, 6 and 8. A more comprehensive set of energy levels is given in the supplementary material.<sup>53</sup> From these tables one can see that the discrepancy between observed and calculated energy values increases both gently and smoothly with rotational quantum number  $J$ . Such calculations therefore provide an excellent starting point for assigning high  $J$  transitions both within the ground state and to excited vibrational states, as the density of observed transitions is orders of magnitude smaller than the accuracy of calculations.

## 4 Conclusions

We present results of *ab initio* and slightly adjusted *ab initio* calculations for the vibrational and rovibrational energy levels of the  $\text{H}_2\text{O}_2$  molecule. Use of the accurate *ab initio* PES calculated by Małyszczek and Koput<sup>16</sup> reproduces the known vibrational band origin with a standard deviation of about 1  $\text{cm}^{-1}$ . The use of programme TROVE<sup>62</sup> for the nuclear motion calculations allowed us compute high rotational levels up to  $J = 35$ . Indeed, energy levels with  $J = 50$  could be calculated on a high-end workstation, and the accuracy of prediction will be very high - better than 0.5  $\text{cm}^{-1}$ . However, we have not yet performed such calculations, as no comparison with experimental values is currently possible. Experimentally derived energy levels up to  $J = 35$  are compared with our calculations. These are reproduced with an unprecedented accuracy of 0.001  $\text{cm}^{-1}$  for the levels up to  $J = 10$  and 0.02  $\text{cm}^{-1}$  for all the known levels above this. Variational calculations using this slightly adjusted *ab initio* PES results in very smooth variation in the discrepancies between the observed and calculated levels as a function of the rotational quantum numbers  $J$  and  $K_a$ . This smoothness and accuracy is the key to the successful analysis of previously unassignable spectra<sup>30,61</sup> as, in particular, the accidental resonances, which seriously complicate any analysis based on the use an effective Hamiltonian, are automatically allowed for in such calculations.

There is one other important aspect of the  $\text{H}_2\text{O}_2$  rotation-vibration problem which we should

mention. The detection of extrasolar planets and, in particular, our ability to probe the molecular composition of these bodies using spectroscopy,<sup>63</sup> has led to demand for accurate, comprehensive line lists over an extended range of both temperature and wavelength for all species of possible importance in exoplanet atmospheres.<sup>64</sup> The accuracy of the calculations presented here and, especially their ability to reliably predict highly excited rotational levels which are of increasing importance at higher temperatures, suggests that the present work will provide an excellent starting point for the calculation of a comprehensive line list for  $\text{H}_2\text{O}_2$ . In this we will be following the recent work of Bowman and co-workers who have computed similar line lists for somewhat more rigid hydrocarbon systems.<sup>65,66</sup>

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Table 1: Calculated and observed energy levels, in  $\text{cm}^{-1}$ , for  $J = 0$  using WAVR4, TROVE and published by Małyszczek and Koput (MK);<sup>16</sup> “tr-shift” results are computed with an adjusted height for the torsional barrier. The observed values are taken from Ref. 35,36,67,68.

$v_1$	$v_2$	$v_3$	$v_4$	$v_5$	$v_6$	Sym	Obs	WAVR4	TROVE	tr-shift	MK
0	0	0	1	0	0	$A_g$	254.550	256.406	256.419	255.490	255.43
0	0	0	2	0	0	$A_g$	569.743	570.334	570.251	570.690	570.45
0	0	1	0	0	0	$A_g$	865.939	865.547	865.652	865.468	866.02
0	0	0	3	0	0	$A_g$	1000.882	1001.227	1001.073	1002.493	1001.92
0	0	0	0	0	1	$B_u$	1264.583	1264.819	1265.121	1264.868	1264.54
0	0	0	1	0	1	$B_u$	1504.872	1505.977	1506.283	1505.634	
0	0	0	2	0	1	$B_u$	1853.634	1853.949	1854.424	1855.305	
0	0	0	0	0	0	$A_u$	11.437	11.014	10.997	11.289	11.28
0	0	0	1	0	0	$A_u$	370.893	371.247	371.203	371.478	371.32
0	0	0	2	0	0	$A_u$	776.122	776.465	776.320	777.336	776.93
0	0	1	0	0	0	$A_u$	877.934	877.094	877.200	877.303	
0	0	0	0	0	1	$B_g$	1285.121	1284.889	1285.249	1285.457	
0	0	0	1	0	1	$B_g$	1648.367	1648.553	1649.012	1649.485	
0	0	0	2	0	1	$B_g$	2072.404	2072.384	2072.949	2074.231	

## References

- [1] D. Davis, *Can. J. Chem.*, 1974, **52**, 1405–1414.
- [2] D. Vione, V. Maurino, C. Minero and E. Pelizzetti, *Annali di Chimica*, 2003, **93**, 477–488.
- [3] N. D. C. Allen, G. G. Abad, P. F. Bernath and C. D. Boone, *J. Quant. Spectrosc. Radiat. Transf.*, 2013, **115**, 66–77.
- [4] T. Encrenaz, B. Bezard, T. K. Greathouse, M. J. Richter, J. H. Lacy, S. K. Atreya, A. S. Wong, S. Lebonnois, F. Lefevre and F. Forget, *Icarus*, 2004, **170**, 424–429.
- [5] T. Encrenaz, T. K. Greathouse, F. Lefevre and S. K. Atreya, *Planet Space Sci.*, 2012, **68**, 3–17.
- [6] P. Bergman, B. Parise, R. Liseau, B. Larsson, H. Olofsson, K. M. Menten and R. Güsten, *Astron. Astrophys.*, 2011, **531**, L8.
- [7] M. J. Bramley and T. Carrington, *J. Chem. Phys.*, 1993, **99**, 8519–8541.

Table 2: Calculated and observed energy levels, in  $\text{cm}^{-1}$ , for the vibrational ground state (left hand column) and the (000 100  $A_g$ ) state - (right hand column) with  $J = 1, 3$  and 5. Observed energy levels taken from Ref. 36.

$J$	$K_a$	$K_c$	Obs	Calc	o-c	Obs	Calc	o-c
1	0	1	1.71154	1.71152	0.00002	256.255	256.255	0.000
1	1	1	10.90677	10.9068	0.0000	265.427	265.427	0.000
1	1	0	10.9426	10.9426	0.0000	265.474	265.475	0.001
3	0	3	10.2683	10.2682	0.0001	264.777	264.777	0.000
3	1	3	19.374	19.374	0.000	273.830	273.831	-0.001
3	1	2	19.589	19.589	0.000	274.119	274.117	0.002
3	2	2	47.115	47.115	0.000	301.555	301.556	0.001
3	2	1	47.115	47.115	0.000	301.556	301.557	0.001
3	3	1	93.155	93.155	0.000	347.509	347.512	0.003
3	3	0	93.155	93.155	0.000	347.509	347.512	0.003
5	0	5	25.6667	25.6664	0.0003	280.113	280.112	0.001
5	1	5	34.613	34.613	0.000	288.954	288.954	0.000
5	1	4	35.151	35.150	0.001	289.671	289.671	0.000
5	2	4	62.513	62.513	0.000	316.893	316.893	0.000
5	2	3	62.517	62.517	0.000	316.899	316.899	0.000
5	3	3	108.551	108.551	0.000	362.845	362.847	0.002
5	3	2	108.551	108.551	0.000	362.845	362.847	0.002
5	4	2	172.968	172.968	0.000	427.143	427.146	0.003
5	4	1	172.968	172.968	0.000	427.143	427.146	0.003
5	5	1	255.733	255.733	0.000	509.757	509.764	0.007
5	5	0	255.733	255.733	0.000	509.757	509.764	0.007

Table 3: Calculated and observed energy levels, in  $\text{cm}^{-1}$ , for the (000 200  $A_g$ ) (left hand column) and the (000 300  $A_g$ ) state - right hand column) with  $J = 1, 3$  and 5. Observed energy levels taken from Ref. 36.

$J$	$K_a$	$K_c$	Obs	Calc	o-c	Obs	Calc	o-c
1	0	1	571.448	571.449	-0.001	1002.584	1002.584	0.000
1	1	1	580.550	580.549	0.001	1011.664	1011.614	0.050
1	1	0	580.577	580.576	0.001	1011.678	1011.628	0.050
3	0	3	579.976	579.975	0.001	1011.098	1011.097	0.001
3	1	3	589.009	589.007	0.002	1020.143	1020.093	0.050
3	1	2	589.174	589.172	0.002	1020.225	1020.176	0.049
3	2	2	616.427	616.427	0.000	1047.246	1047.244	0.002
3	2	1	616.427	616.427	0.000	1047.246	1047.244	0.002
3	3	1	661.974	661.975	0.001	1092.462	1092.411	0.051
3	3	0	661.974	661.975	0.001	1092.462	1092.411	0.051
5	0	5	595.324	595.324	0.000	1026.421	1026.021	0.008
5	1	5	604.235	604.232	0.003	1035.404	1035.354	0.050
5	1	4	604.645	604.644	0.001	1035.610	1035.561	0.049
5	2	4	631.773	631.773	0.000	1062.566	1062.565	0.001
5	2	3	631.775	631.775	0.000	1062.566	1062.565	0.001
5	3	3	677.317	677.315	0.002	1107.779	1107.729	0.050
5	3	2	677.317	677.315	0.002	1107.779	1107.729	0.050
5	4	2	741.046	741.044	0.002	1170.935	1170.930	0.005
5	4	1	741.046	741.044	0.002	1170.935	1170.930	0.005
5	5	1	822.934	822.930	0.004	1252.191	1252.140	0.051
5	5	0	822.934	822.930	0.004	1252.191	1252.140	0.051

Table 4: Calculated and observed energy levels, in  $\text{cm}^{-1}$ , for the (001 000  $A_g$ ) (left hand column) and the (000 000  $A_u$ ) state - right hand column) with  $J = 1, 3$  and 5. Observed energy levels taken from Ref. 36.

$J$	$K_a$	$K_c$	Obs	Calc	o-c	Obs	Calc	o-c
1	0	1	867.628	867.628	0.000	13.150	13.149	0.001
1	1	0	876.815	876.816	0.001	22.337	22.337	0.000
1	1	0	876.851	876.850	0.001	22.369	21.368	0.001
3	0	3	876.074	875.073	0.001	21.712	21.711	0.001
3	1	3	885.171	884.171	0.000	30.821	30.820	0.001
3	1	2	885.386	885.387	-0.001	31.009	31.009	0.000
3	2	2	912.886	912.885	0.001	58.518	58.518	0.000
3	2	1	912.887	912.887	0.000	58.518	58.518	0.000
3	3	1	958.884	958.887	-0.003	104.508	104.508	0.000
3	3	0	958.884	958.887	-0.003	104.508	104.508	0.000
5	0	5	891.273	891.2712	0.002	37.121	37.120	0.001
5	1	5	900.210	900.209	0.001	46.089	46.088	0.001
5	1	4	900.749	900.748	0.001	46.561	46.560	0.001
5	2	4	928.085	928.085	0.000	73.926	73.926	0.000
5	2	3	928.089	928.088	0.001	73.929	73.928	0.001
5	3	3	974.080	974.082	-0.002	119.913	119.913	0.000
5	3	2	974.080	974.082	-0.002	119.913	119.913	0.000
5	4	2	1038.438	1038.440	-0.002	184.260	184.261	-0.001
5	5	1	1121.127	1121.133	-0.006	266.936	266.938	-0.002

Table 5: Calculated and observed energy levels, in  $\text{cm}^{-1}$ , for the (000 100  $A_u$ ) (left hand column) and the (000 200  $A_u$ ) state - (right hand column) with  $J = 1, 3$  and 5. Observed energy levels taken from the Ref. 36.

$J$	$K_a$	$K_c$	Obs	Calc	o-c	Obs	Calc	o-c
1	0	0	372.601	372.602	0.001	777.826	777.827	-0.001
1	1	1	381.733	381.733	0.000	786.881	786.891	-0.010
1	1	1	381.764	381.764	0.000	786.901	786.911	-0.010
3	0	3	381.140	381.139	0.001	786.350	786.350	0.000
3	1	3	390.195	390.195	0.000	795.355	795.365	-0.010
3	1	2	390.378	390.376	0.002	795.472	795.482	-0.010
3	2	2	417.723	417.722	0.001	822.639	822.640	-0.001
3	2	1	417.723	417.722	0.001	822.639	822.640	-0.001
3	3	1	463.434	463.434	0.000	867.976	867.986	-0.010
3	3	0	463.434	463.434	0.000	867.976	867.986	-0.010
5	0	5	396.505	396.504	0.001	801.689	801.689	0.000
5	1	5	405.426	405.423	0.003	810.607	810.617	-0.010
5	1	4	405.881	405.879	0.002	810.900	810.909	-0.009
5	2	4	433.088	433.088	0.000	837.977	837.977	0.000
5	2	3	433.090	433.089	0.001	837.977	837.977	0.000
5	3	3	478.796	478.794	0.002	883.310	883.320	-0.010
5	3	2	478.796	478.794	0.002	883.310	883.320	-0.010
5	4	2	542.756	542.756	0.000	946.769	946.770	0.001
5	5	1	624.938	624.937	0.001	1028.289	1028.299	-0.010

Table 6: Calculated and observed energy levels, in  $\text{cm}^{-1}$ , for  $J = 30$ . Results are for the ground vibrational state (left hand column) and the  $(000\ 100\ A_g)$  state - (right hand column). Observed energy levels taken from the Ref. 36.

$J$	$K_a$	$K_c$	Obs	Calc	o-c	Obs	Calc	o-c
30	0	30	789.577	789.581	-0.004	1038.983	1038.925	0.058
30	1	30	793.053	793.065	-0.012	1041.540	1041.481	0.039
30	1	29	809.594	809.565	0.029	1063.053	1063.007	0.046
30	2	29	829.292	829.282	0.010	1080.396	1080.345	0.051
30	2	28	832.547	832.521	0.026	1086.079	1086.036	0.043
30	3	28	876.030	876.017	0.013	1127.862	1127.815	0.047
30	3	27	876.191	876.174	0.017	1128.304	1128.262	0.042
30	4	27	940.027	940.015	0.012	1191.838	1191.794	0.044
30	4	26	940.029	940.013	0.016	1191.850	1191.807	0.043
30	5	26	1022.323	1022.311	0.012	1274.332	1274.293	0.039
30	5	25	1022.324	1022.312	0.012	1274.332	1274.293	0.039
30	6	25	1122.848	1122.837	0.011	1371.047	1371.024	0.023
30	6	24	1122.849	1122.838	0.011	1371.047	1371.024	0.023
30	7	24	1241.304	1241.294	0.010	1491.957	1491.933	0.024
30	7	23	1241.304	1241.294	0.010	1491.957	1491.933	0.024
30	8	23	1381.938	1381.916	0.022	1628.749	1628.731	0.018
30	9	21	1534.588	1534.578	0.010	1782.735	1782.739	-0.004
30	10	21	1707.358	1707.349	0.009	1958.577	1958.558	0.019
30	11	19	1898.169	1898.159	0.010	2148.182	2148.186	-0.004



Table 7: Calculated and observed energy levels, in  $\text{cm}^{-1}$ , for  $J = 30$  levels of the (000 000  $A_u$ ) vibrational state. Observed energy levels taken from Ref. 36.

$J$	$K_a$	$K_c$	Obs	Calc	o-c
30	0	30	802.349	802.340	0.009
30	1	30	806.280	806.276	0.004
30	1	29	820.768	820.746	0.022
30	2	29	841.344	841.330	0.013
30	2	28	843.911	843.892	0.019
30	3	28	887.854	887.839	0.015
30	3	27	887.964	887.949	0.015
30	4	27	951.826	951.815	0.011
30	4	26	951.828	951.817	0.011
30	5	26	1034.096	1034.085	0.011
30	5	25	1034.096	1034.085	0.011
30	5	25	1134.609	1134.599	0.010
30	5	24	1253.291	1253.284	0.007
30	5	24	1390.060	1390.055	0.005
30	5	23	1544.803	1544.803	0.000
30	5	23	1717.164	1717.167	-0.003

Table 8: Variationally calculated and observed or predicted using effective Hamiltonian) energy levels, in  $\text{cm}^{-1}$ , for  $J = 35$ . Observed energy levels taken from the Ref. 36.

$J$	$K_a$	$K_c$	Obs	Calc	o-c	Obs	Calc	o-c
35	0	35	1067.027	1067.037	-0.010	1314.205	1314.124	0.081
35	1	35	1069.466	1069.484	-0.018	1315.869	1315.787	0.082
35	1	34	1091.715	1091.680	0.035	1344.395	1344.338	0.057
35	2	34	1108.893	1108.882	0.011	1358.709	1358.637	0.052
35	2	33	1114.564	1114.523	0.041	1368.256	1368.203	0.053
35	3	33	1156.257	1156.241	0.016	1407.374	1407.309	0.065
35	3	32	1156.655	1156.628	0.027	1408.434	1408.382	0.052
35	4	32	1220.062	1220.044	0.018	1471.314	1471.252	0.062
35	4	31	1220.070	1220.051	0.019	1471.355	1471.296	0.059
35	5	31	1302.102	1302.088	0.014	1553.875	1553.821	0.054
35	5	30	1302.114	1302.098	0.016	1553.876	1555.822	0.054
35	6	30	1402.366	1402.353	0.013	1648.318	1648.288	0.030
35	6	29	1402.369	1402.350	0.019	1648.318	1648.288	0.030
35	7	29	1520.294	1520.282	0.012	1769.879	1769.844	0.035
35	8	28	1662.739	1662.707	0.032	1906.483	1906.459	0.024
35	9	27	1814.222	1814.207	0.015			
35	10	26	1986.565	1986.552	0.013			

Table 9: Variationally calculated and observed or predicted using effective Hamiltonian) energy levels, in  $\text{cm}^{-1}$ , for  $J = 35$

$J$	$K_a$	$K_c$	Obs	Calc	o-c	Obs	Calc	o-c
35	0	35	1933.163	1932.118	0.045	1080.587	1080.574	0.013
35	1	35	1936.042	1935.996	0.046	1083.472	1083.465	0.007
35	1	34	1955.496	1955.415	0.081 u	1102.961	1102.929	0.032
35	2	34	1973.810	1973.743	0.067 u	1121.270	1121.247	0.023
35	2	33	1978.296	1978.228	0.068 u	1125.774	1125.743	0.031
35	3	33	2020.807	2020.749	0.058 u	1168.268	1168.245	0.023
35	3	32	2021.078	2021.020	0.058 u	1168.540	1168.517	0.023
35	4	32	2084.733	2084.691	0.042 u	1232.076	1232.060	0.016
35	4	31	2084.738	2084.768	0.042 u	1232.081	1232.055	0.026
35	5	31	2165.503	2165.420	0.083 u	1314.156	1314.138	0.018
35	5	30	2165.503	2165.420	0.083 u	1314.156	1314.138	0.018
						1414.475	1414.459	0.016
						1532.940	1532.928	0.012
						1669.447	1669.438	0.009
						1823.841	1823.839	0.002

- [8] S. Carter and N. C. Handy, *J. Chem. Phys.*, 2000, **113**, 987–993.
- [9] D. Luckhaus, *J. Chem. Phys.*, 2000, **113**, 1329–1347.
- [10] R. Q. Chen, G. B. Ma and H. Guo, *J. Chem. Phys.*, 2001, **114**, 4763–4774.
- [11] H. G. Yu and J. T. Muckerman, *J. Mol. Spectrosc.*, 2002, **214**, 11–20.
- [12] M. Mladenovic, *Spectra Chimica Acta A*, 2002, **58**, 809–824.
- [13] S. Y. Lin and H. Guo, *J. Chem. Phys.*, 2003, **119**, 5867–5873.
- [14] S. Carter, N. C. Handy and J. M. Bowman, *Mol. Phys.*, 2009, **107**, 727–737.
- [15] S. Carter, A. R. Sharma and J. M. Bowman, *J. Chem. Phys.*, 2011, **135**, 014308.
- [16] P. Małyszekk and J. Koput, *J. Comput. Chem.*, 2012, **xxx**, in press, DOI: 10.1002/jcc.23137.
- [17] L. B. Harding, *J. Phys. Chem.*, 1991, **95**, 8653–8660.
- [18] B. Kuhn, T. R. Rizzo, D. Luckhaus, M. Quack and M. A. Suhm, *J. Chem. Phys.*, 1999, **111**, 2565–2587.
- [19] M. Senent, S. Fernandez-Herrera and Y. Smeyers, *Spectra Chimica Acta A*, 2000, **56**, 1457–1468.
- [20] J. Koput, S. Carter and N. C. Handy, *J. Chem. Phys.*, 1998, **102**, 6325–6335.
- [21] T. M. Ticich and T. R. Rizzo, *J. Chem. Phys.*, 1986, **84**, 1508–1520.
- [22] O. L. Polyansky, A. G. Császár, S. V. Shirin, N. F. Zobov, P. Barletta, J. Tennyson, D. W. Schwenke and P. J. Knowles, *Science*, 2003, **299**, 539–542.
- [23] M. Pavanello, L. Adamowicz, A. Alijah, N. F. Zobov, I. I. Mizus, O. L. Polyansky, J. Tennyson, T. Szidarovszky, A. G. Császár, M. Berg, A. Petrigani and A. Wolf, *Phys. Rev. Lett.*, 2012, **108**, 023002.
- [24] X. Huang, D. W. Schwenke, S. A. Tashkun and T. J. Lee, *J. Chem. Phys.*, 2012, **136**, 124311.
- [25] X. Huang, D. W. Schwenke and T. J. Lee, *J. Chem. Phys.*, 2011, **134**, 044320.
- [26] X. Huang, D. W. Schwenke and T. J. Lee, *J. Chem. Phys.*, 2011, **134**, 044321.
- [27] P. Drossart, J. P. Maillard, J. Caldwell, S. J. Kim, J. K. G. Watson, W. A. Majewski, J. Tennyson, S. Miller, S. Atreya, J. Clarke, J. H. Waite Jr. and R. Wagener, *Nature*, 1989, **340**, 539–541.

- [28] S. S. Lee, B. F. Ventrudo, D. T. Cassidy, T. Oka, S. Miller and J. Tennyson, *J. Mol. Spectrosc.*, 1991, **145**, 222–224.
- [29] B. M. Dinelli, L. Neale, O. L. Polyansky and J. Tennyson, *J. Molec. Spectrosc.*, 1997, **181**, 142–150.
- [30] O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath and L. Wallace, *Science*, 1997, **277**, 346–349.
- [31] O. L. Polyansky, N. F. Zobov, S. Viti and J. Tennyson, *J. Mol. Spectrosc.*, 1998, **189**, 291–300.
- [32] L. A. Zumwalt and P. A. Giguere, *J. Chem. Phys.*, 1941, **9**, 458–462.
- [33] P. A. Giguere, *J. Chem. Phys.*, 1950, **18**, 88–92.
- [34] W. B. Olson, R. H. Hunt, B. W. Young, A. G. Maki and J. W. Brault, *J. Mol. Spectrosc.*, 1988, **127**, 12–34.
- [35] A. Perrin, J.-M. Flaud, C. Camy-Peyret, A. Goldman, F. J. Murcray and R. D. Blatherwick, *J. Mol. Spectrosc.*, 1990, **142**, 129–147.
- [36] C. Camy-Peyret, J.-M. Flaud, J. W. C. Johns and M. Noel, *J. Mol. Spectrosc.*, 1992, **155**, 84–104.
- [37] S. N. Yurchenko, R. J. Barber, A. Yachmenev, W. Thiel, P. Jensen and J. Tennyson, *J. Phys. Chem. A*, 2009, **113**, 11845–11855.
- [38] S. N. Yurchenko, R. J. Barber and J. Tennyson, *Mon. Not. R. Astr. Soc.*, 2011, **413**, 1828–1834.
- [39] K. Sung, L. R. Brown, X. Huang, D. W. Schwenke, T. J. Lee, S. L. Coy and K. K. Lehmann, *J. Quant. Spectrosc. Radiat. Transf.*, 2012, **113**, 1066–1083.
- [40] N. F. Zobov, S. V. Shirin, R. I. Ovsyannikov, O. L. Polyansky, S. N. Yurchenko, R. J. Barber, J. Tennyson, R. Hargreaves and P. Bernath, *J. Mol. Spectrosc.*, 2011, **269**, 104–108.
- [41] M. J. Down, C. Hill, S. N. Yurchenko, J. Tennyson, L. R. Brown and I. Kleiner, *J. Quant. Spectrosc. Radiat. Transf.*, 2013.
- [42] S. Carter and J. M. Bowman, *J. Chem. Phys.*, 1998, **108**, 4397–4404.
- [43] S. N. Yurchenko, W. Thiel and P. Jensen, *J. Mol. Spectrosc.*, 2007, **245**, 126 –140.
- [44] I. N. Kozin, M. M. Law, J. M. Hutson and J. Tennyson, *J. Chem. Phys.*, 2003, **118**, 4896–4904.
- [45] L. Lodi, J. Tennyson and O. L. Polyansky, *J. Chem. Phys.*, 2011, **135**, 034113.

- [46] I. N. Kozin, M. M. Law, J. Tennyson and J. M. Hutson, *Comput. Phys. Commun.*, 2004, **163**, 117–131.
- [47] J. Koput, S. Carter and N. C. Handy, *J. Chem. Phys.*, 2001, **115**, 8345–8350.
- [48] J. Cizek, *J. Chem. Phys.*, 1966, **45**, 4256–4266.
- [49] G. Scuseria and T. Lee, *J. Chem. Phys.*, 1990, **93**, 5851–5855.
- [50] J. Noga and W. Kutzelnigg, *J. Chem. Phys.*, 1994, **101**, 7738–7762.
- [51] MOLPRO (version 2002.1) is a package of *ab initio* electronic structure programs designed by H.-J. Werner and P. J. Knowles.
- [52] G. Simons, R. Parr and J. Finlan, *J. Chem. Phys.*, 1973, **59**, 3229–3234.
- [53] Supplemented masterial.
- [54] I. N. Kozin, M. M. Law, J. Tennyson and J. M. Hutson, *J. Chem. Phys.*, 2005, **122**, 064309.
- [55] A. Urru, I. N. Kozin, G. Mulas, B. J. Braams and J. Tennyson, *Mol. Phys.*, 2010, **108**, 1973–1990.
- [56] J. T. Hougen, *Can. J. Phys.*, 1984, **62**, 1392–1402.
- [57] P. Jensen and P. R. Bunker, *Molecular Symmetry and Spectroscopy*, NRC, Canada, 1998.
- [58] B. Numerov, *Mon. Not. R. Astron. Soc.*, 1924, **84**, 592–xxx.
- [59] J. W. Cooley, *Math. Comp.*, 1961, **15**, 363–374.
- [60] J. Tennyson and B. T. Sutcliffe, *J. Chem. Phys.*, 1982, **77**, 4061–4072.
- [61] O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath and L. Wallace, *Astrophys. J.*, 1997, **489**, L205–L208.
- [62] S. Yurchenko, P. Jensen and W. Thiel, *J. Chem. Phys.*, 2004, **71**, 281–291.
- [63] G. Tinetti, A. Vidal-Madjar, M.-C. Liang, J.-P. Beaulieu, Y. Yung, S. Carey, R. J. Barber, J. Tennyson, I. Ribas, N. Allard, G. E. Ballester, D. K. Sing and F. Selsis, *Nature*, 2007, **448**, 169–171.
- [64] J. Tennyson and S. N. Yurchenko, *Mon. Not. R. Astr. Soc.*, 2012, **425**, 21–33.
- [65] R. Warmbier, R. Schneider, A. R. Sharma, B. J. Braams, J. M. Bowman and P. H. Hauschildt, *Astron. Astrophys.*, 2009, **495**, 655–661.

- [66] S. Carter, A. R. Sharma and J. M. Bowman, *J. Chem. Phys.*, 2012, **137**, 154301.
- [67] J.-M. Flaud, C. Camy-Peyret, J. W. C. Johns and B. Carli, *J. Chem. Phys.*, 1989, **91**, 1504–1510.
- [68] A. Perrin, A. Valentin, J. M. Flaud, C. Camy-Peyret, L. Schriver, A. Schriver and P. Arcas, *J. Mol. Spectrosc.*, 1995, **171**, 358–373.